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(71) Applicant *(for all designated States except US)*: CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH–4057 Basel (CH).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: PUEBLA, Claudio [CL/DE]; Arend–Braye–Strasse 42, D–79540 Lörrach (DE). KASCHIG, Jürgen [DE/DE]; Rötebuckweg 30, D–79104 Freiburg (DE). TRABER, Rainer, Hans [DE/CH]; Im Stockacker 26, CH–4153 Reinach (CH).

(74) Common Representative: CIBA SPECIALTY CHEMICALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH–4057 Basel (CH).

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(54) Title: THE USE OF A BRIGHTENER PIGMENT IN DETERGENTS OR CLEANSERS

(57) Abstract

The use of a brightener pigment comprising (a) a water–insoluble urea–formaldehyde resin and (b) a water–soluble fluorescent whitening agent. The brightener pigments are used for the purpose of improving the appearance of detergents, of compounds thereof, and of individual raw materials. The fluorescent whitening agent does not contact the goods being washed. Depending on the final use, the brightener pigment is subjected to a surface treatment.

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The use of a brightener pigment in detergents or cleanseres

The present invention relates to the use of a brightener pigment comprising
(a) a water-insoluble polymer compound and
(b) a water-soluble fluorescent whitening agent
for increasing the degree of whiteness of detergents or cleansers, of compounds thereof and of individual raw materials.

Component (a) may be, for example, a highly-disperse, solid polymer compound formed by polymerisation, polycondensation or by polyaddition reactions or by a combination of such reactions. Such polymer compounds are described in GB-A-1 323 890 and include condensation polymers, especially aminoplastic condensation polymers, such as, for example, urea-formaldehyde and melamine-formaldehyde polymer compounds, and also vinyl polymers, such as, for example, polyacrylonitrile.

Preferably, there is used in accordance with the invention a water-insoluble urea-formaldehyde resin of which the molar ratio of urea to formaldehyde is preferably from 1:1.3 to 2 moles. The urea-formaldehyde resin is also distinguished by a small particle diameter of from 2 to 10 μm and a low BET specific surface area of from 15 to 120 m^2/g.

The BET specific surface area of the preferred water-insoluble urea-formaldehyde resins is ascertained according to the Brunauer, Emmett and Teller method [cf. J.Am.Chem.Soc. 60, 309-319 (1938), Chemie-Ing.Techn. 32, 349-354 (1960) and 35, 568-589 (1963)] according to DIN 66132.

The preferred water-insoluble urea-formaldehyde resins, which correspond to component (a), and the preparation of those polymers, are known, for example, from A. Renner: Makromolekulare Chemie 149, 1-27 (1971).

The preferred component (a) compounds are prepared by reacting formaldehyde with urea in aqueous solution in the above-described ratios. The reaction is carried out preferably in two steps. In the first reaction step, urea is reacted with formaldehyde according to a customary condensation mechanism, resulting in a low-molecular-weight, water-soluble pre-condensate. In the second reaction step, an acid catalyst can be used in order to accelerate

the reaction and for crosslinking, an insoluble, finely divided solid being obtained.

The water content of the reaction solution should never be lower than the total weight of the reactants present in the reaction mixture, and should be higher than the total weight of all the other components in the reaction mixture during the precipitation of the insoluble polymer particles.

The reaction temperature in the first reaction step is usually in the range from 20 to 100°C. The pH can be adjusted to from 6 to 9 by the addition of a strong, aqueous, inorganic base, such as, for example, sodium hydroxide solution.

Advantageously, the preparation of the pre-condensate can be carried out in the presence of a surfactant. The surfactant is used, for example, in amounts of from 0.5 to 5 % by weight, based on the total weight of the urea and formaldehyde. Ionic surfactants cause an increase in the specific surface area of the urea-formaldehyde polymer product, whereas non-ionic surfactants have the opposite effect.

Advantageously, the first reaction step is carried out in the presence of a macromolecular water-soluble protective colloid having polyelectrolytic properties. Examples of such protective colloids include gelatin, tragacanth, agar and polyvinylpyrrolidone, especially methacrylic acid. The amount of protective colloid used can be within a range of, for example, from 0.5 to 5 % by weight, based on the total weight of urea and formaldehyde. Neither polyvinylpyrrolidone nor polymethacrylic acid causes an increase in the specific surface area of the water-insoluble urea-formaldehyde resin.

One of the most important conditions for the successful preparation of non-meltable, insoluble and finely divided urea-formaldehyde polymers that meet the qualitative requirements of the brightener pigments used in accordance with the invention is the use in the second reaction step of a suitable catalyst for gel formation. Suitable catalysts include, for example, relatively strong inorganic and/or organic acids, such as, for example, sulfuric acid, sulfurous acid, sulfamic acid, phosphoric acid, hydrochloric acid, chloroacetic acid, maleic acid or maleic anhydride. Generally, such gel-formation catalysts should have an ionisation constant in excess of 10^{-4}. Sulfuric acid and its acidic ammonium or amine salts, and also ammonium sulfate, methylamine hydrogen sulfate and ethanolamine hydrogen

sulfate, are preferred. The acids are generally used in the form of 1 to 15 % by weight aqueous solutions. As a rough guide, from 20 to 100 mmoles of a crosslinking catalyst are used per mole of urea added. This causes a reduction in the pH of the reaction mixture to from 1 to 3.0 in the second reaction step during the formation of the polymer.

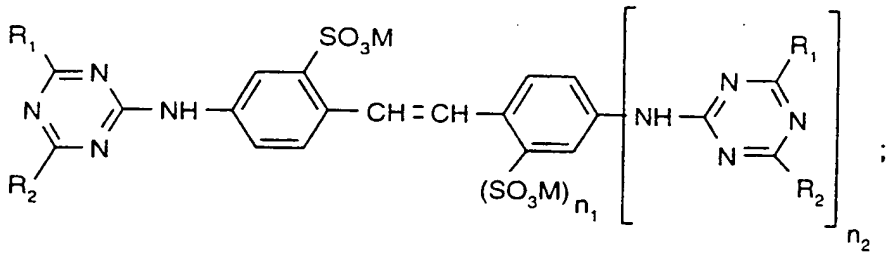
When sulfamic acid is used, water-insoluble urea-formaldehyde resins having a relatively high specific surface area are generally obtained, the other acids of those mentioned above, especially sulfuric acid and its ammonium or amine salts, having the opposite effect.

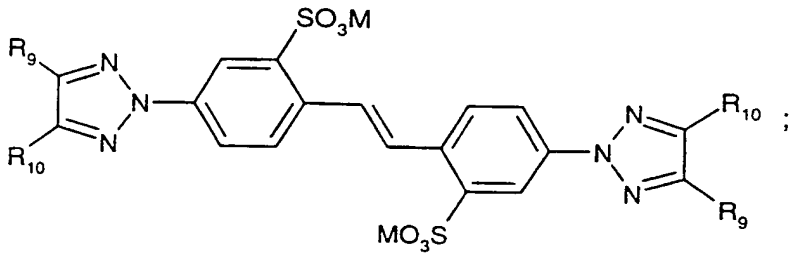
The reaction temperatures in the second, resin-forming reaction step usually reach from 20 to 100°C. Large differences in temperature in the reaction mixture should be avoided during the addition of the catalyst. It is therefore desirable to heat the aqueous catalyst solution to the temperature of the reaction mixture before it is added to that mixture. Generally, a white gel is obtained after only from 15 to 30 seconds. The crosslinking reaction is usually finished after a reaction time of from 30 minutes to 3 hours.

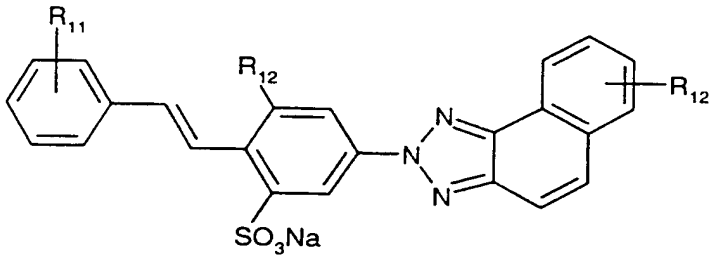
The insoluble polymer is obtained in the form of a white gel and can be comminuted mechanically, treated with an approximately equal amount of water, adjusted with alkali or ammonium hydroxide to a pH of from 6 to 9, and then isolated from the aqueous phase, for example by filtration, centrifugation or concentration by evaporation. The drying can be carried out e.g. by spray-drying or convection-drying.

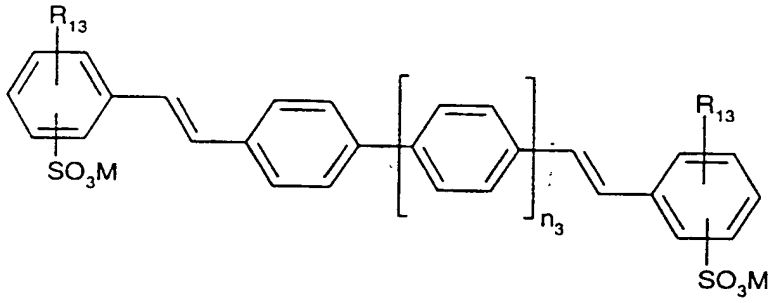
The gel obtained is then worked up in customary manner, for example by allowing the reaction to proceed to completion, neutralising, where appropriate adding one or more of the fluorescent whitening agents mentioned hereinbelow in cases where the addition of the fluorescent whitening agent is not undertaken until after gelation, and then filtering, washing, drying and, if desired, grinding to obtain a suitable particle size.

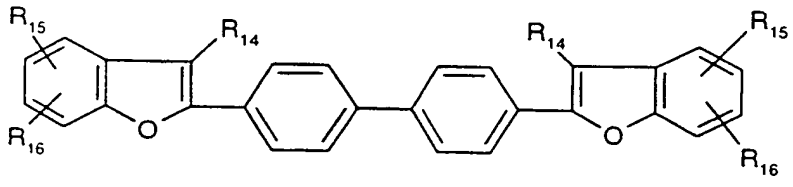
Preferred fluorescent whitening agents corresponding to component (b) that can be used in accordance with the invention correspond to formula

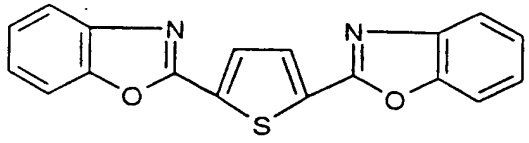
(1) 

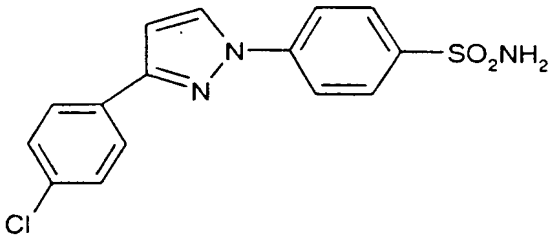
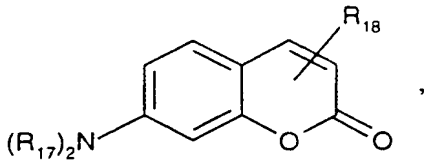
(2) 

(3) 

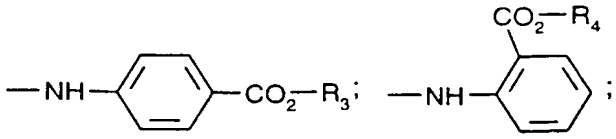
(4) 

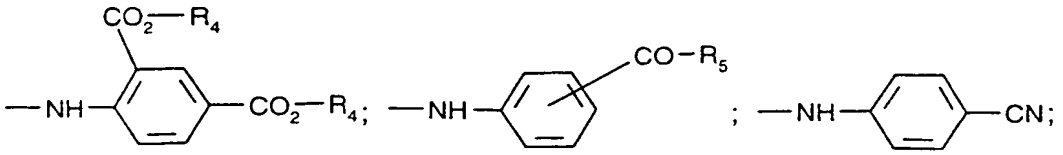
(5) 

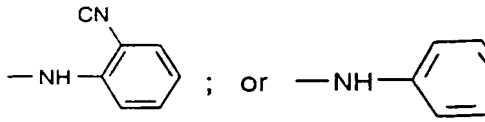
(6) 

(7)  ; or (8)  ,

in which formulae

R_1 is a radical of formula 



 ; or ;

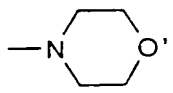
R_3 is an unsubstituted or substituted alkyl or aryl group;

R_4 is M, or an unsubstituted or substituted alkyl or aryl group;

R_5 is hydrogen; an unsubstituted or substituted alkyl or aryl group; or $-NR_7R_8$, wherein R_7 and R_8 are each independently of the other hydrogen or an unsubstituted or substituted alkyl or aryl group, or R_7 and R_8 together with the nitrogen atom linking them form a heterocyclic radical, especially a morpholino or piperidino radical;

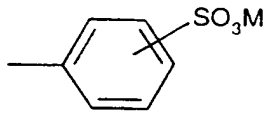
R_6 is hydrogen, or an unsubstituted or substituted alkyl or aryl group;

R_2 is hydrogen; an unsubstituted or substituted alkyl or aryl group; or a radical of formula

 , -OH, $-NH_2$, $-N(CH_2CH_2OH)_2$, $-N[CH_2CH(OH)CH_3]_2$, -NH-R_4, $-N(R_4)_2$ or $-OR_4$; or

R_1 and R_2 are each independently of the other -OH, -Cl, $-NH_2$, -O-C_1-C_4alkyl, -O-aryl, -NH-C_1-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$, $-N(C_1$-C_4alkyl$)(C_1$-C_4hydroxyalkyl), $-N(C_1$-C_4hydroxyalkyl$)_2$, -NH-aryl, morpholino or -S-C_1-C_4alkyl(aryl);

R_9 and R_{10} are each independently of the other hydrogen, C_1-C_4alkyl, phenyl or a radical of

formula  ;

R_{11} is hydrogen, -Cl or SO_3M;

R_{12} is -CN, - SO_3M, -S(C_1-C_4alkyl)$_2$ or -S(aryl)$_2$;

R_{13} is hydrogen, -SO_3M, -O-C_1-C_4alkyl, -CN, -Cl, -COO-C_1-C_4alkyl or -CON(C_1-C_4alkyl)$_2$;

R_{14} is hydrogen, -C_1-C_4alkyl, -Cl or -SO_3M;

R_{15} and R_{16} are each independently of the other hydrogen, C_1-C_4alkyl, -SO_3M, -Cl or -O-C_1-C_4alkyl;

R_{17} is hydrogen or C_1-C_4alkyl;

R_{18} is hydrogen, C_1-C_4alkyl, -CN, -Cl, -COO-C_1-C_4alkyl, -CON(C_1-C_4alkyl)$_2$, aryl or -O-aryl;

M is hydrogen, sodium, potassium, calcium, magnesium, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium, mono-, di- or tri-C_1-C_4hydroxyalkylammonium, or ammonium di- or tri-substituted by a mixture of C_1-C_4alkyl and C_1-C_4hydroxyalkyl groups; and

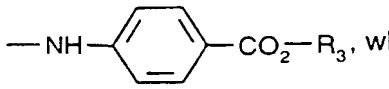
n_1, n_2 and n_3 are each independently of the others 0 or 1.

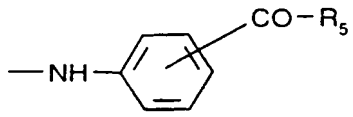
R_2, R_3, R_4, R_5, R_6, R_7 and R_8 representing (unsubstituted or) substituted alkyl are each C_1-C_{12}alkyl, preferably C_1-C_4alkyl. The alkyl groups may be branched or unbranched and may be unsubstituted or substituted by halogen, e.g. fluorine, chlorine or bromine, by C_1-C_4alkoxy, e.g. methoxy or ethoxy, by phenyl or carboxyl, by C_1-C_4alkoxycarbonyl, e.g. acetyl, by mono- or di-C_1-C_4alkylamino or by -SO_3M.

R_2, R_3, R_4, R_5, R_6, R_7 and R_8 representing (unsubstituted or) substituted aryl are each preferably a phenyl or naphthyl group that may be unsubstituted or substituted by C_1-C_4alkyl, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl, by C_1-C_4alkoxy, e.g. methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy or tert-butoxy, by halogen, e.g. fluorine, chlorine or bromine, by C_2-C_5alkanoylamino, e.g. acetylamino, propionylamino or butyrylamino, by nitro, by sulfo or by di-C_1-C_4alkylated amino.

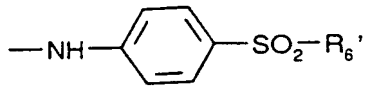
The compounds of formula (1) are used preferably in neutral form, that is to say:
M is preferably a cation of an alkali metal, especially sodium, or is an amine.

In the compounds of formula (1), R_1 is preferably a radical of formula

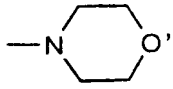
 , wherein R_3 is as defined above and is preferably C_1-C_4alkyl,

especially methyl or ethyl; or a radical of formula  , wherein R_5 is as

defined above and is preferably C_1-C_4alkyl, especially methyl or ethyl, or $-NR_7R_8$, wherein R_7 and R_8 are as defined above and are preferably hydrogen, C_1-C_4alkyl, especially methyl or ethyl, or a morpholino or piperidino radical, more especially hydrogen; or a radical of formula

 , wherein R_6 is as defined above and is preferably C_1-C_4alkyl

substituted by $-SO_3M$, especially methyl or ethyl substituted by $-SO_3M$, wherein M is as defined above and is preferably sodium; and

R_2 is preferably  , $-NH_2$, $-N(CH_2CH_2OH)_2$ or $-N[CH_2CH(OH)CH_3]_2$.

The compounds of formula (1) can be prepared under known reaction conditions by reacting cyanuric chloride with the corresponding aminostilbenesulfonic acids and an amino compound that is capable of introducing a group R_1, and with a compound that is capable of introducing a group R_2, wherein R_1 and R_2 are as defined above.

The fluorescent whitening agents that can be used advantageously in the present invention are listed by way of example in the following Table 1:

Table 1:

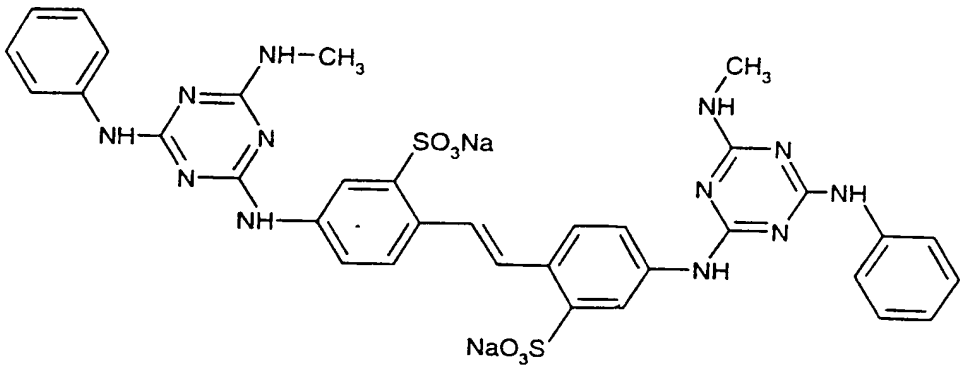
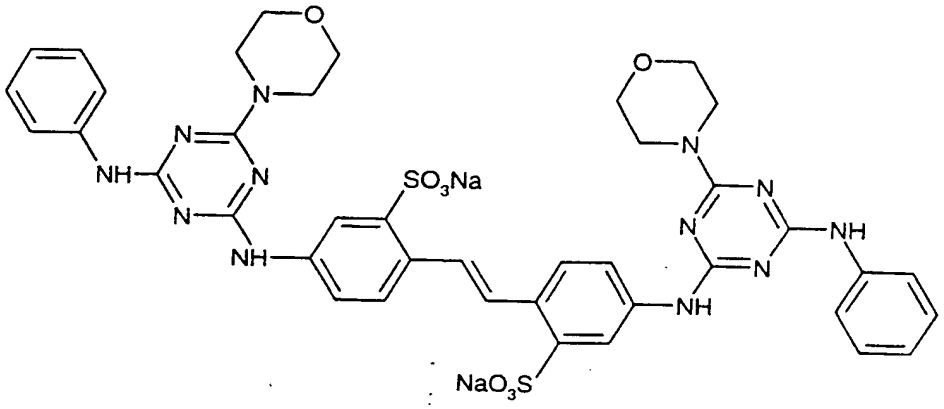
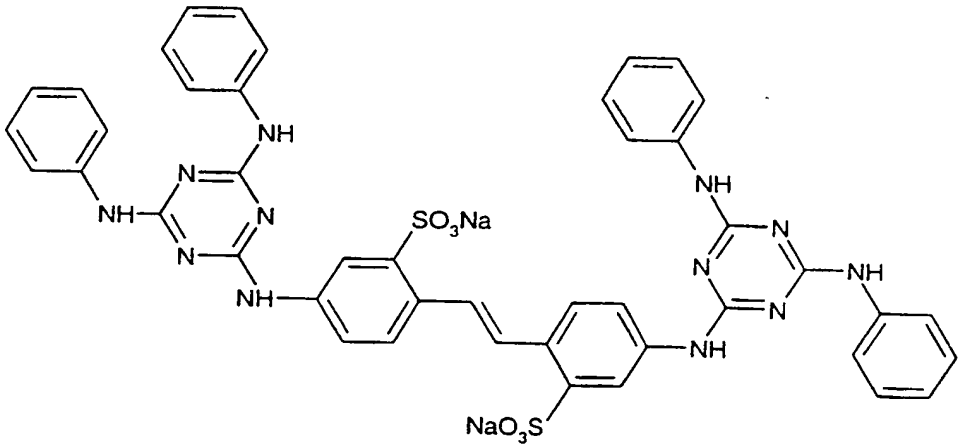
Compound of formula	
(9)	
(10)	
(11)	

Table 1:	
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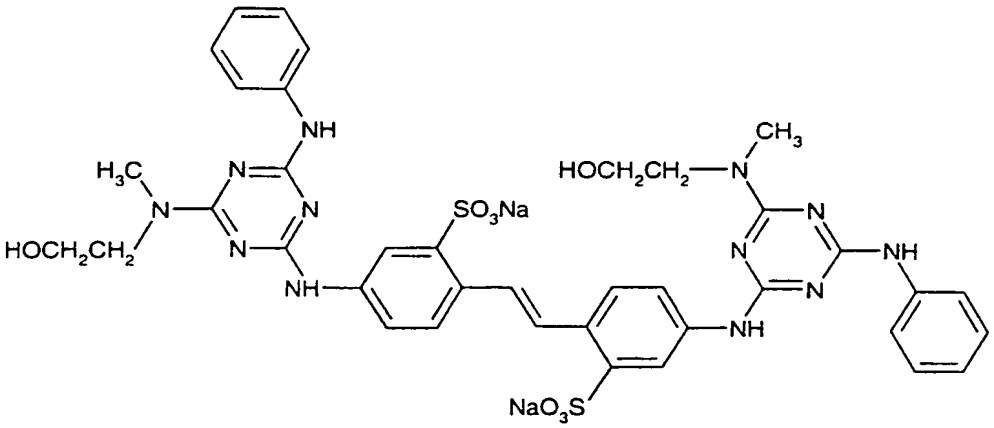
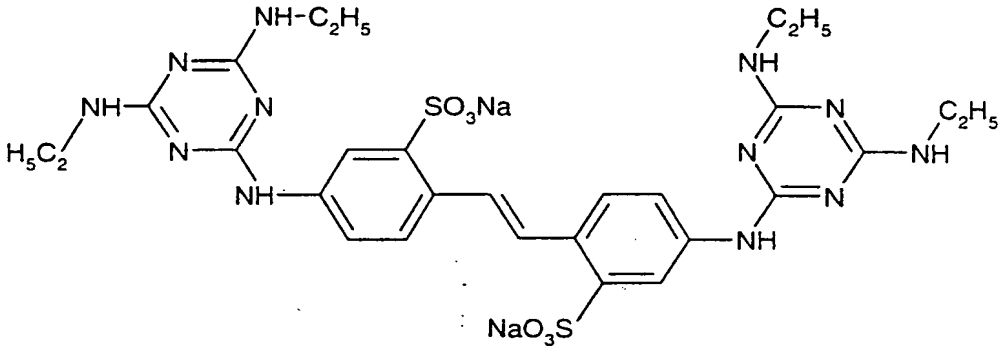
(12)	
(13)	

Table 1:

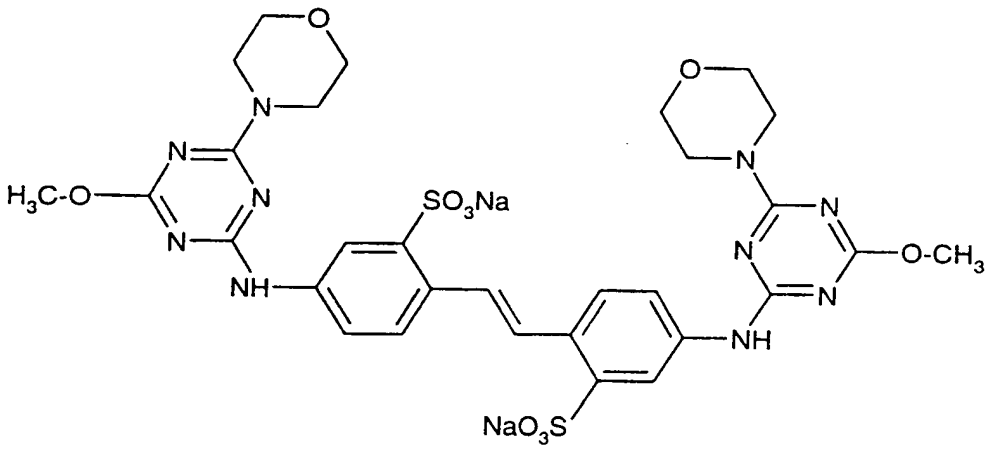
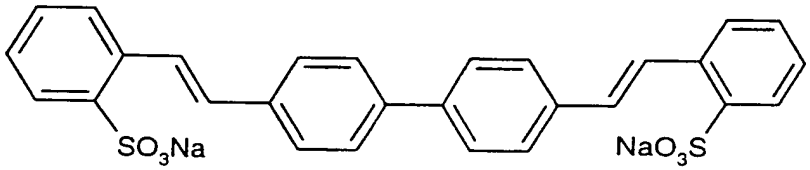
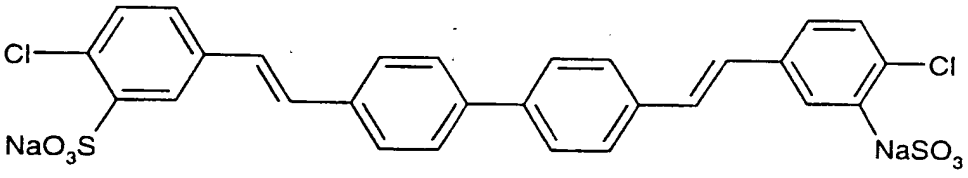
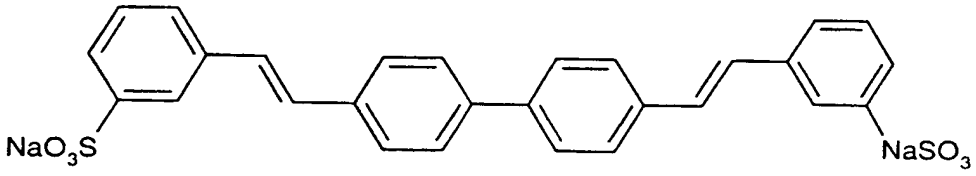
Compound of formula	
(14)	
(15)	
(16)	
(17)	

Table 1:

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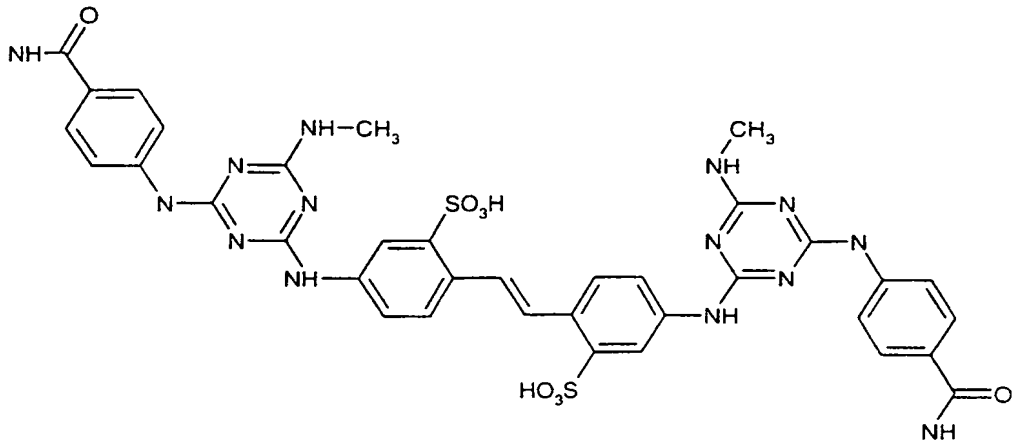
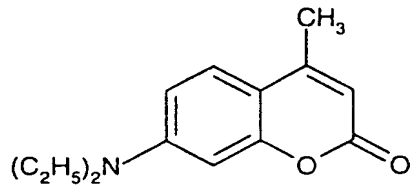
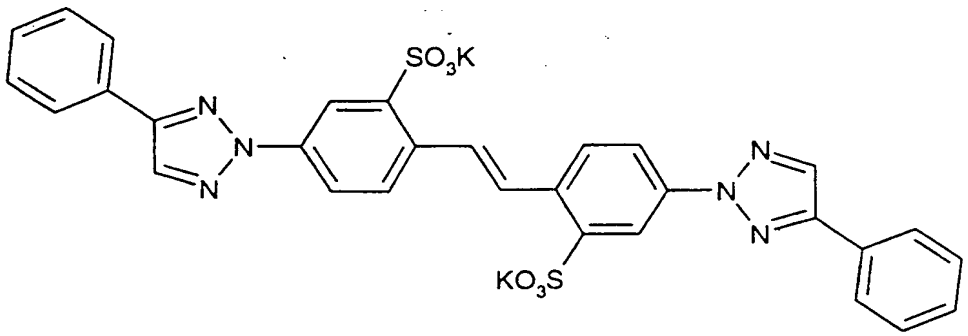
(18)	
(19)	
(20)	

Table 1:

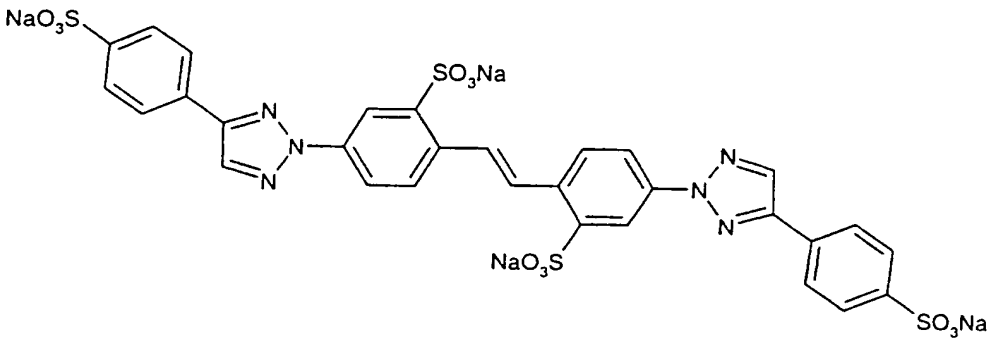
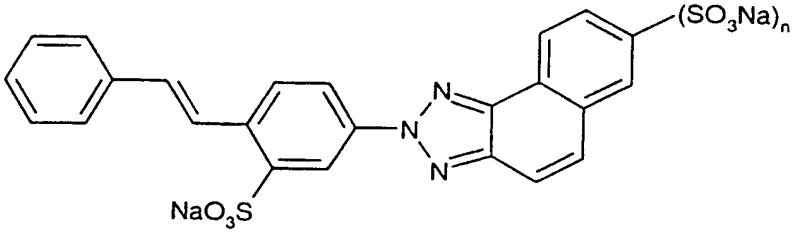
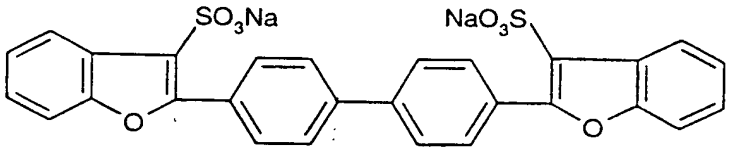
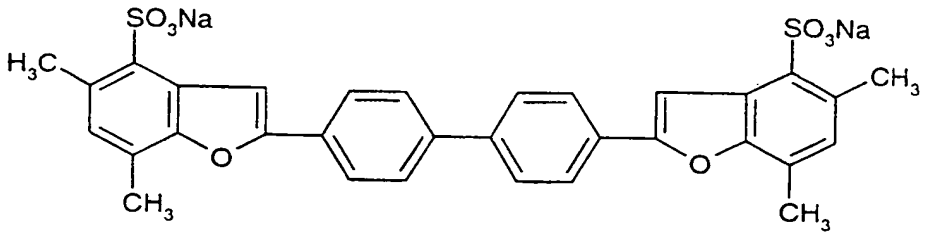
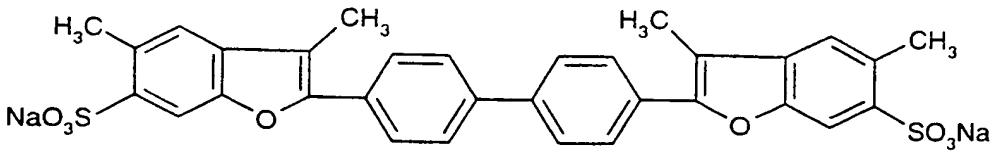
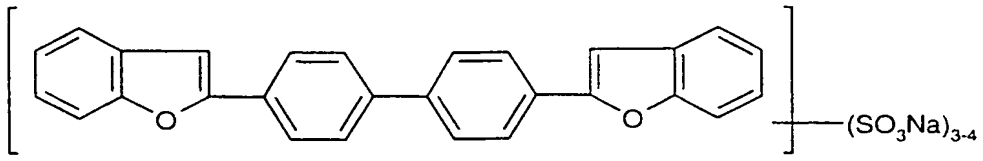
Compound of formula	
(21)	
(22)	
(23)	
(24)	
(25)	

Table 1:	
Compound of formula	
(26)	

The fluorescent whitening agents corresponding to component (b) used in accordance with the invention are employed preferably in amounts of from 0.001 to 1.0 % by weight, especially from 0.01 to 0.5 % by weight, and more especially from 0.01 to 0.5 % by weight, based on the total amount of urea-formaldehyde resin. The fluorescent whitening agents can be added to the urea-formaldehyde resin in the form of individual compounds or in the form of mixtures of several individual compounds.

The brightener pigment used in accordance with the invention comprising components (a) and (b) can, in principle, be used for whitening detergents or cleansers on its own or together with other pigments. Other pigments that can be used include, e.g., talc, titanium dioxide, aluminium oxide, aluminium hydroxide, zinc oxide, chalk, zeolite or clays, e.g. kaolin.

The brightener pigment used in accordance with the invention is usually prepared by adding the water-soluble fluorescent whitening agent before, during or after gelation. Usually, the procedure comprises dispersing the urea-formaldehyde resin in hot water with a vigorous stirring action. The pH is adjusted to <10 using an aqueous alkali metal hydroxide solution and the water-soluble fluorescent whitening agent is added thereto. The batch is further stirred for some time, cooled, and the pH is adjusted to <3 using a strong acid, especially sulfuric acid. A viscous suspension is obtained which is further processed by customary methods, such as filtration, drying and, if desired, grinding.

In a further embodiment, the brightener pigment may be subjected to a surface treatment. For that purpose, an emulsion of long-chain alcohols or derivatives thereof, of derivatives of ethylene oxide-alcohols, of paraffin waxes, or of hydrogenated natural or synthetic resins,

etc., and especially a dodecanol emulsion, is added to the viscous urea-formaldehyde resin/whitening agent suspension. The batch is stirred for a further 10 to 15 minutes at elevated temperature. After cooling, the batch is filtered, dried and ground in customary manner, yielding a surface-treated formaldehyde resin/whitening agent suspension.

Dazzlingly white organic brightener pigments are obtained which have a very low content of free formaldehyde (typically less than 0.1% DIN 58187) in which the fluorescent whitening agent has been incorporated or adsorbed. Such products are solid, colloidal particles having an average diameter of from 0.1 to 0.2 μm, which are agglomerated to form pigment particles having an average diameter of from 3 to 20 μm.

The fluoresecently brightened pigments prepared in that manner are excellently suitable for improving the degree of whiteness (improvement in appearance) of commerically available detergents and cleansers, of compounds thereof, and of individual raw materials.

The brightener pigment used in accordance with the invention is usually incorporated into the detergents or cleansers by first suspending the brightener pigment in water, with stirring, and then adding the detergent or cleanser in question to the resulting suspension with the further addition of water. A creamy slurry is obtained, which is then dried and sieved to yield a detergent or cleanser having a particle size of approximately from > 0.3 to 1 mm.

In a further embodiment, the fluorescently brightened detergent or cleanser, compounds thereof and individual raw materials are prepared by simply dusting with the brightener pigment in powder form. For that purpose from 0.5 to 20%, typically from 1 to 10%, of brightener pigment based on the component to be whitened is dry-mixed until the particles have been coated with the pigment.

Suitable compositions that can be treated in accordance with the invention with the brightener pigment comprising components (a) and (b) are detergents or cleansers in the form of powder or granules. Such formulations may be particulate detergents composed of one or more granular components in which at least one granular component is acted upon by the brightener pigment.

There come into consideration preferably formulations in granular form that have a high bulk

density. In addition to the brightener pigment, the detergent may comprise further ingredients, e.g. surfactants, inorganic and organic builder substances, bleaching agents, substances that have a positive effect on the ability to wash out oil and grease, greying inhibitors, if desired substances that improve the solubility and the rate of dissolution of the individual granular components and/or of the entire formulations, fabric-softening substances, colorants and perfumes, and also alkaline and/or neutral salts in the form of their sodium and/or potassium salts.

In addition, washing-active or cleaning-active shaped forms, for example detergent tablets, dishwashing agent tablets, stain-removing salt tablets or water-softening tablets, can be provided in accordance with the invention.

The washing-active or cleaning-active shaped forms are especially cylindrical shapes or tablets that can be used as detergents, dishwashing agents, or bleaching agents (stain-removing salts), but can also be used as pretreatment agents, for example as water softeners or bleaching agents. A distinction is drawn between homogeneous (homogeneously distributed ingredients) and heterogeneous (heterogenously distributed ingredients) shaped forms, which have as a special feature a disintegrator, such as, for example, starch, a starch derivative, cellulose or a cellulose derivative, which brings about the disintegration of the washing-active or cleaning-active shaped form. It is possible, in particular, for the degree of whiteness of such a disintegrator to be excellently improved by the brightener pigments used in accordance with the invention.

The so-treated detergent is distinguished by a very high degree of whiteness, which is substantially higher than that achieved by the discrete addition of organic white pigment and fluorescent whitening agent.

A further advantage of the detergent or cleanser treated in such a manner is that, during the actual washing operation, the brightener pigment or the fluorescent whitening agent does not contact and is not absorbed by the goods being washed.

The following Examples illustrate the invention, without the invention being limited thereto.

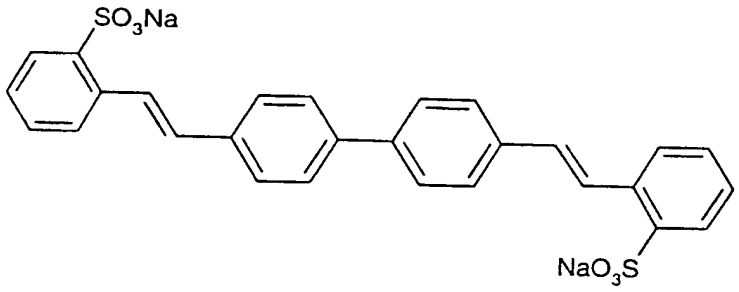
Example 1:

a. Preparation of a urea-formaldehyde condensation polymer/whitening agent suspension

500 ml of water are taken as the initial component and heated to 70°C.

100 g of a commercially available urea-formaldehyde condensation polymer (e.g. Pergopack® M2) are suspended in the water and stirred vigorously to achieve a homogeneous distribution. A pH of 10 is established using sodium hydroxide.

1.5 g of the fluorescent whitening agent of formula

(101) 

are then added and the batch is stirred for a further 10 minutes. With further stirring, the batch is allowed to cool to 60°C.

b. Surface-treatment and isolation

The suspension prepared in Step a. is adjusted to a pH of 2.5 using 1N sulfuric acid and heated to 60°C. Since the solution becomes very viscous, vigorous stirring is necessary.

A dodecanol suspension is then prepared by taking 500 ml of water, heating the water to 90°C, and adding 1 g of dodecane-1,2-diol with stirring and while cooling to 60°C. The dodecanol suspension is added at 60°C, with vigorous stirring, to the prepared whitening agent suspension. The solution slowly becomes very liquid.

The solution is stirred for a further 10 minutes at 60°C and is cooled with vigorous stirring and subsequently filtered (amount of filtrate: 500 ml).

The filter cake is dried at 60°C and finely ground.

Approximately 110 g of a white, finely powdered product are obtained.

Degree of whiteness of the filtered product: approximately 233 points (degree of whiteness according to Ganz) and 163 points (CIE).

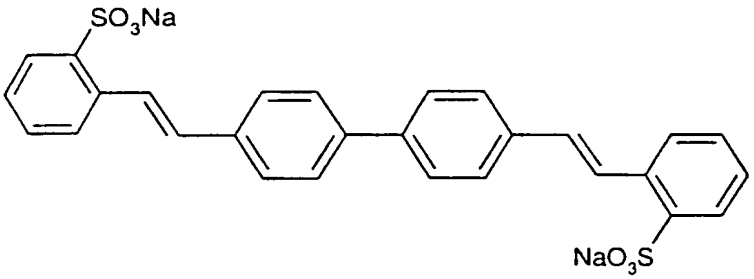
Example 2:

a. Preparation of a urea-formaldehyde condensation polymer/whitening agent suspension

60.0 kg of demineralised water are taken as the initial component and heated to from 65 to 70°C.

10.0 kg of a commercially available urea-formaldehyde condensation polymer (e.g. Pergopack® M2) are suspended in the water and stirred vigorously to achieve a homogeneous distribution. A pH of 10 is established using 0.12 kg of 1N sodium hydroxide solution.

0.187 kg of the fluorescent whitening agent of formula

(101) 

is added and the batch is stirred for a further 10 minutes at from 65 to 70°C.
The pH is then adjusted to 7 using 0.07 kg of 2N sulfuric acid, and subsequently 4.0 kg of sodium chloride are introduced and the batch is stirred for a further 30 minutes at from 65 to 70°C.

b. Surface-treatment and isolation

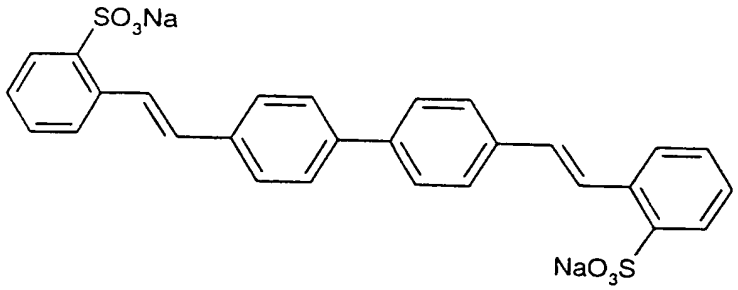
20.0 kg of demineralised water are introduced into a vessel and heated to from 65 to 70°C. 0.10 kg of 1,2-dodecanediol is then added and the batch is stirred for at least 10 minutes. The resulting emulsion is then added to the suspension prepared in Step a., and the dispersion is stirred for 10 minutes at 60°C and then cooled to a temperature of <40°C. Filtration is then carried out, and the filter cake is dried at 60°C and finely ground.

Example 3:

a. Preparation of a urea-formaldehyde condensation polymer/whitening agent suspension

400 ml of demineralised water are taken as the initial component and, with stirring, adjusted to pH 10.4 by the addition of 1N sodium hydroxide solution and heated to 69°C.

8.0 g of the fluorescent whitening agent of formula

(101) 

are then added. With stirring, 100.0 g of a commercially available urea-formaldehyde condensation polymer (e.g. Pergopack® M2) are added to the resulting solution, yielding a thick suspension. A pH of 10 is established using 0.12 kg of 1N sodium hydroxide solution. A further 400 ml of demineralised water that has previously been adjusted to pH 10.4 by the addition of 1N sodium hydroxide solution and subsequently heated to 60°C is then added. The suspension is stirred for a further 20 minutes at from 65 to 70°C and then the pH is adjusted to 7 by the addition of 2N sulfuric acid.

b. Surface-treatment and isolation

400 ml of demineralised water are taken as the initial component and heated to 90°C. 1.0 g of 1,2-dodecanediol is then added and, with vigorous stirring, allowed to cool to 60°C. The resulting emulsion is then added to the suspension prepared in Step a., which has been heated to 60°C, and the dispersion is stirred for 10 minutes at 60°C and then allowed to cool to a temperature of <40°C. The batch is filtered and the filter cake is dried at 60°C and finely ground.

Application Example

100 g of a detergent formulation having an improved appearance are prepared using

(A) 1.481 g of the white pigment prepared in Example 1,

(B) 98.51 g of ECE detergent formulation and

(C) from 50 to 60 ml of deionised water.

In a porcelain dish, (A) is suspended in approximately 20 ml of deionised water, with stirring, using a pestle.

(B) is gradually added and stirred in. A creamy slurry is formed to which a further 30 to 40 ml of deionised water is added in portions. The resulting smooth slurry is transferred to a

shallow porcelain dish and dried for approximately 14 hours in a vacuum cabinet at 60°C and from 425 to 475 mbar.

After drying, the mass is cooled to room temperature and sieved. The first sieve has a mesh size of from 0.315 to 0.8 mm, and the second a mesh size of < 0.315 mm. Powder having a particle size of < 0.315 mm is discarded.

The detergent formulation having the desired particle size (0.315 to 0.8 mm) is filled into brown glass bottles.

Measurement of the appearance of the washing powder

At least 5.5 g of the prepared detergent formulation are conditioned overnight (at least 20 hours) in a controlled environment chamber. The conditions are 25°C and 65 % relative humidity.

After the conditioning, a tablet is formed by compression and the degree of whiteness according to Ganz is determined.

Execution of washing tests

Test washing machine: Linitest

Washing is carried out under the following conditions:

dosage:	30 g of detergent per kg of fabric
liquor:	5:1 (5 ml of tap water per g of fabric)
washing temperature:	30°C
number of wash cycles:	3
fabric:	10 g of bleached cotton (Co-Renforcé)
drying:	ironing

The washing results (determination of the degree of whiteness) are listed in Table 2:

Table 2:				
Detergent formulated with	Conc. [%]	Degree of whiteness of detergent	Degree of whiteness of fabric after 1 wash cycle	Degree of whiteness of fabric after 3 wash cycles
brightener pigment according to Example 1	1.48	158	76	85
compound of formula (101) *via* slurry	0.02	172	99	125
pigment without whitening agent	1.48	59	72	73

The results in Table 2 show, on the one hand, that the degree of whiteness of the detergent is markedly increased by the brightener pigment used in accordance with the invention and hence results in a considerable improvement in its appearance and, on the other hand, that the material being washed is not affected by the fluorescent whitening agent used.

What is claimed is:

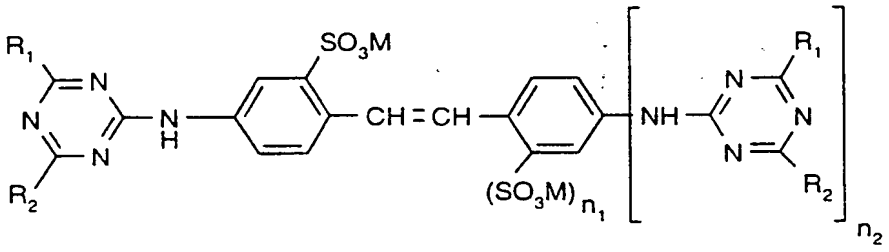
1. Use of a brightener pigment comprising
(a) a water-insoluble polymer compound and
(b) a water-soluble fluorescent whitening agent,
for increasing the degree of whiteness of detergents or cleansers, of compounds thereof, and of individual raw materials.

2. A use according to claim 1, wherein component (a) is selected from aminoplastic condensation polymers and vinyl polymers.

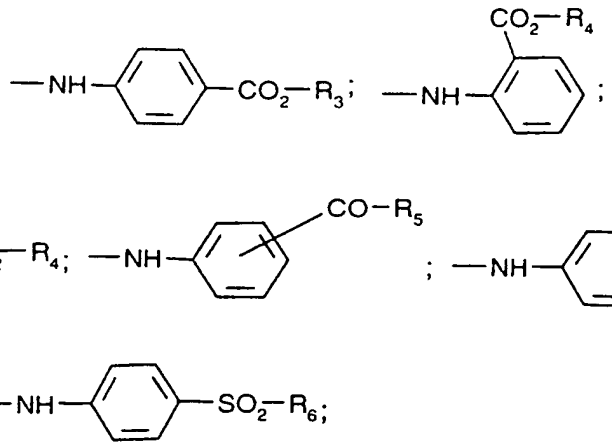
3. A use according to either claim 1 or claim 2, wherein a water-insoluble urea-formaldehyde resin is used as component (a).

4. A use according to claim 3, wherein the water-insoluble urea-formaldehyde resin has a molar ratio of urea to formaldehyde of from 1:1.3 to 2 moles, a particle diameter of from 2 to 10 μm and a BET specific surface area of from 15 to 120 m^2/g.

5. A use according to any one of claims 1 to 4, wherein there is used as component (b) a fluorescent whitening agent of formula

(1) 

wherein

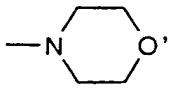
R_1 is a radical of formula 

R_3 is an unsubstituted or substituted alkyl or aryl group;

R_4 is M, or an unsubstituted or substituted alkyl or aryl group;

R_5 is hydrogen; an unsubstituted or substituted alkyl or aryl group; or $-NR_7R_8$, wherein R_7 and R_8 are each independently of the other hydrogen or an unsubstituted or substituted alkyl or aryl group, or R_7 and R_8 together with the nitrogen atom linking them form a heterocyclic radical, especially a morpholino or piperidino radical;

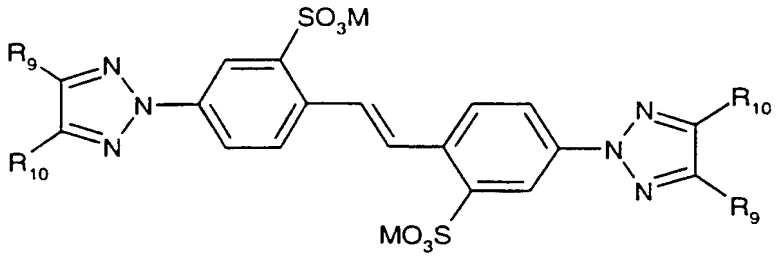
R_6 is hydrogen, or an unsubstituted or substituted alkyl or aryl group,

R_2 is hydrogen; an unsubstituted or substituted alkyl or aryl group; or a radical of formula  , -OH, $-NH_2$, $-N(CH_2CH_2OH)_2$, $-N[CH_2CH(OH)CH_3]_2$, $-NH-R_4$, $-N(R_4)_2$ or $-OR_4$; or

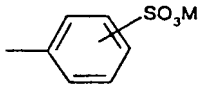
R_1 and R_2 are each independently of the other -OH, -Cl, $-NH_2$, $-O-C_1-C_4$alkyl, -O-aryl, $-NH-C_1-C_4$alkyl, $-N(C_1-C_4alkyl)_2$, $-N(C_1-C_4alkyl)(C_1-C_4hydroxyalkyl)$, $-N(C_1-C_4hydroxyalkyl)_2$, -NH-aryl, morpholino or $-S-C_1-C_4$alkyl(aryl), and

n_1 and n_2 are each independently of the other 0 or 1.

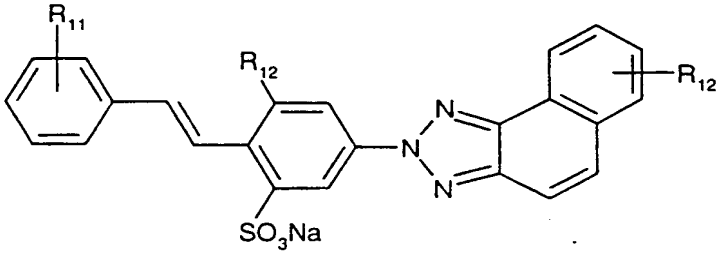
6. A use according to any one of claims 1 to 4, wherein there is used as component (b) a fluorescent whitening agent of formula

(2) 

wherein

R_9 and R_{10} are each independently of the other hydrogen, C_1-C_4alkyl, phenyl or a radical of formula  .

7. A use according to any one of claims 1 to 4, wherein there is used as component (b) a fluorescent whitening agent of formula

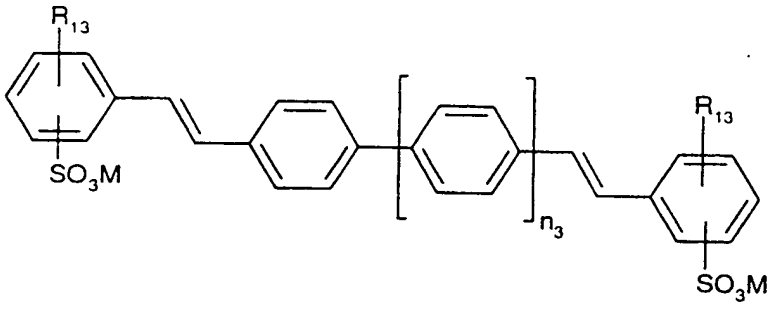
(3) 

wherein

R_{11} is hydrogen, -Cl or -SO_3M; and

R_{12} is -CN, - SO_3M, -S(C_1-C_4alkyl)$_2$ or -S(aryl)$_2$.

8. A use according to any one of claims 1 to 4, wherein there is used as component (b) a fluorescent whitening agent of formula

(4) 

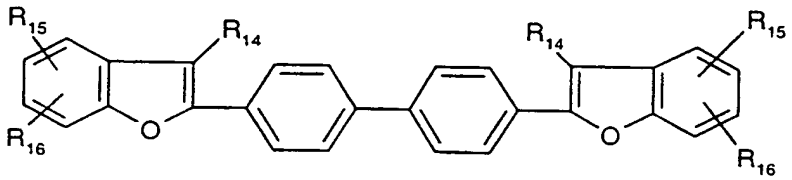
wherein

R_{13} is hydrogen, $-SO_3M$, $-O-C_1-C_4$alkyl, -CN, -Cl, $-COO-C_1-C_4$alkyl or $-CON(C_1-C_4alkyl)_2$;

n_3 is 0 or 1; and

M is as defined in claim 1.

9. A use according to any one of claims 1 to 4, wherein there is used as component (b) a fluorescent whitening agent of formula

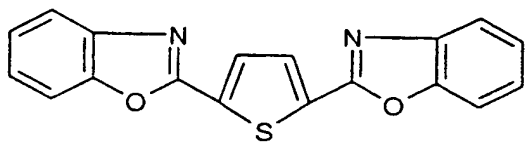
(5) 

wherein

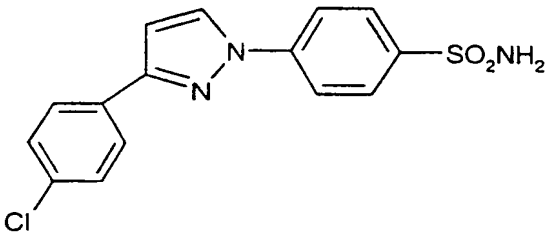
R_{14} is hydrogen, C_1-C_4alkyl, -Cl or $-SO_3M$; and

R_{15} and R_{16} are each independently of the other hydrogen, C_1-C_4alkyl, $-SO_3M$, -Cl or $-O-C_1-C_4$alkyl.

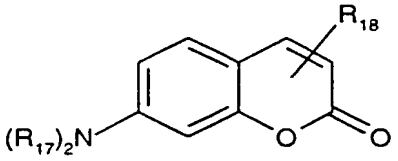
10. A use according to any one of claims 1 to 4, wherein there is used as component (b) a fluorescent whitening agent of formula

(6) 

11. A use according to any one of claims 1 to 4, wherein there is used as component (b) a fluorescent whitening agent of formula

(7) 

12. A use according to any one of claims 1 to 4, wherein there is used as component (b) a fluorescent whitening agent of formula

(8) 

wherein

R_{17} is hydrogen or C_1-C_4alkyl; and

R_{18} is hydrogen, C_1-C_4alkyl, -CN, -Cl, -COO-C_1-C_4alkyl, -CON(C_1-C_4alkyl)$_2$, aryl or -O-aryl.

13. A use according to any one of claims 1 to 12, which comprises subjecting the pigment obtained from components (a) and (b) to a subsequent treatment with an emulsion of long-chain alcohols or derivatives thereof, of derivatives of ethylene oxide-alcohols, of paraffin waxes, or of hydrogenated natural or synthetic resins.

14. A use according to claim 13, wherein the emulsion consists of long-chain alcohols, especially dodecanol.

15. A use according to any one of claims 1 to 14, wherein there are used, as detergents or cleansers, formulations in powder or granular form or washing-active or cleaning-active shaped forms.

16 A use according to any one of claims 1 to 14, wherein compounds and individual raw materials of detergents or cleansers are used.

17. A method of preparing a brightener pigment comprising
(a) a water-insoluble urea-formaldehyde resin and
(b) a water-soluble fluorescent whitening agent,
which comprises adding together (a) and (b) and subsequently treating the urea-formaldehyde/whitening agent suspension with an emulsion of long-chain alcohols or derivatives thereof, of derivatives of ethylene oxide-alcohols, of paraffin waxes, or of hydrogenated natural or synthetic resins.

18. A method according to claim 17, which comprises carrying out the subsequent surface treatment with a dodecanol emulsion.

INTERNATIONAL SEARCH REPORT

Inte. onal Application No
PCT/EP 00/02459

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/42 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	EP 0 900 783 A (CIBA GEIGY AG) 10 March 1999 (1999-03-10) claims 1,8-23 examples 13,18 page 3, line 8 - line 29 ---	1-4,8, 15,16 5-7, 9-14,17, 18
X A	GB 2 213 161 A (PROCTER & GAMBLE) 9 August 1989 (1989-08-09) claims examples I-VI page 2, line 13 - line 33 page 3, line 17 - line 31 page 4, line 22 -page 6, line 23 page 7, line 9 - line 19 --- -/--	1-3,15, 16 4-14,17, 18

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search	Date of mailing of the international search report
20 July 2000	28/07/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Neys, P

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INTERNATIONAL SEARCH REPORT

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